Synchronous SIM/Scan Low-Level PAH Analysis Using the Agilent Technologies 6890/5975 inert GC/MSD

Application

Environmental

Author

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Abstract

The analysis of Polynuclear Aromatic Hydrocarbons (PAHs) presents challenges due to the tendency of the PAHs to adsorb on surfaces in the chromatographic system. Selected Ion Monitoring (SIM) analysis is needed for low-level analysis, while scan data are desired for confirmation. The 6890/5975 inert GC/MSD system is designed for improved PAH analysis using synchronous SIM/scan while maintaining linearity across a wide calibration range.

Introduction

PAHs are produced during combustion of organic material and are suspected carcinogens. The high amounts and widespread occurrence of these compounds in our environment requires reliable, sensitive, and very robust analytical methods.

PAHs tend to be adsorbed on any active or cold site in a GC/MSD system, such as inlets and ion sources. The 6890/5975 inert includes the inert source with high temperature filaments described previously [1]. Using the proper inlet liner also improves chromatographic peak shape and sensitivity.

Many laboratories calibrate for PAHs from 0.1 ppm to 10 ppm using SIM for low-level work. Historically, SIM has been necessary because of instrument sensitivity and loss of PAHs at the lower concentration levels. Full scan data is preferred for further confirmation of the compounds. The 5975 inert can acquire both SIM and scan data in a single run.

This application note will show the performance of the 6890/5975 inert for PAHs using a calibration range of 0.01 ppm–10.0 ppm in synchronous SIM/scan mode with linearity equal to that of many SIM only methods.

Instrument Operating Parameters

The recommended instrument operating parameters are listed in Table 1. These are starting conditions and may have to be optimized.

Table 1. Gas Chromatograph and Mass Spectrometer Conditions

GC	Agilent Technologies 6890			
Inlet	EPC Split/Splitless			
Mode	Pulsed Splitless, 1 µL injected			
Inlet temp	300 °C			
Pressure	13.00 psi			
Pulse pressure	40.0 psi			
Pulse time	0.20 min			
Purge flow	30.0 mL/min			
Purge time	0.75 min			
Total flow	34.6 mL/min			
Gas saver	Off			
Gas type	Helium			
Inlet Liner	**Description**			**Agilent part number**
	Direct connect, dual-taper, 4-mm id			G1544-80700
	or Splitless liner, single-taper, 4-mm id			5181-3316
Oven 240 V				
Oven ramp	**°C/min**	**Next °C**	**Hold min**	
Initial		55	1.00	
Ramp 1	25	320	3.00	
Total run time	14.60 min			
Equilibration time	0.5 min			
Oven max temp	325 °C			
Column	Agilent Technologies HP-5MS			19091S-433
Length	30.0 m			
Diameter	250 µm			
Film thickness	0.25 µm			
Mode	Constant Flow = 1.5 mL/min			
Inlet	Front			
Outlet	MSD			
Outlet pressure	Vacuum			
RTL	System Retention Time Locked to Triphenyl phosphate at 10.530 min			
MSD	Agilent Technologies 5975			
Drawout lens	6-mm ultra-large aperture			G2589-20045
Solvent delay	4.00 min			
EM voltage	Run at Autotune voltage = 1294 V			
Low mass scan	45 amu			
High mass scan	450 amu			
SIM	12 groups, 3–6 ions/group, 10 ms dwell/ion			
Threshold	0			
Sampling	1			
Cycles/s	5.55 each, SIM and scan			
Quad temp	180 °C			
Source temp	300 °C			
Transfer line temp	280 °C			
Emission current	Autotune value = 34.6 µamp			

Calibration Standards

Calibration standards were diluted in dichloromethane from a stock mix of 16 PAHs. The 10 levels made were 10, 5, 2, 1, 0.5, 0.2, 0.1, 0.05, 0.02 and 0.01 ppm. The perylene-d12 internal standard and the three surrogate standards, 1,3-dimethyl-2-nitrobenzene, pyrene-d10 and triphenylphosphate, were added to each calibration level at 1.0 ppm.

The 6890 inlet temperature was set to 300 °C, instead of the typical 250 °C, to minimize compounds adsorbing on the liner surface. Pulsed injection was used to facilitate quantitative transfer of the heavier PAHs onto the column, minimizing inlet discrimination. Pulsed injection parameters are easily set in the ChemStation software and are automatically controlled by the EPC (Electronic Pneumatic Control) module.

The Direct Connect inlet liner allows for complete transfer of analytes onto the column. The column inlet end attaches to the liner and minimizes analyte exposure to the stainless steel annular volume in the inlet. The splitless liner, 5181-3316, yields better peak shapes for early eluters at the expense of lower amounts of analytes transferred to the column. Neither of these liners is well suited for split injections. Higher concentration samples requiring split injection would need a cyclosplitter-type liner, also suitable for splitless.

The 6890N 240V oven was necessary for the 25 °C/min ramp used up to the final temperature of 320 °C. A 120 V oven will achieve 20 °C/min at these higher temperatures and could be used, resulting in slightly longer run times.

The HP-5MS column is the most widely used column for environmental analysis. It has excellent lifetime and stability at elevated temperatures.

The system was Retention Time Locked to Triphenyl phosphate at 10.530 min. See the fundamentals of Retention Time Locking (RTL) for GC/MSD systems [2]. The primary benefit of RTL for the environmental laboratory is the ability to maintain retention times after clipping or changing the column. Quant database and integration events times do not have to be changed. For laboratories performing PAH SIM analyses, reproducible retention times are a must so SIM group times remain constant. Additional RTL application notes are available at www.agilent.com/chem, detailing the numerous benefits of RTL.

The 5975 inert was tuned using Autotune. The automatic DFTPP target tune, as required by some government methods, can also be used. The ultra-large aperture drawout lens was used to maintain linearity across the wide calibration range of 0.01–10.0 ppm. Source temperature was set to 300 °C, which is now possible with the high temperature filaments. This higher source temperature in combination with the new source material produces better peak shapes for the PAHs.

Data were collected using the synchronous SIM/scan mode available with the 5975 inert. A quant database is first setup using full scan data. SIM ions and groups are then determined automatically using Generate AutoSIM Method. A checkbox in data acqusition is used to acquire SIM and scan data in the same run. For details of synchronous SIM/scan, see reference 3.

Results

The system was calibrated at 10 levels: 0.01, 0.02, 0.05, 0.1, 0.2, 0.5, 1.0, 2.0, 5.0, and 10.0 ppm using the SIM data from SIM/scan acquisition. The calibration table allows the user to choose either the SIM or scan data. The TIC (Total Ion Chromatogram) for the 0.2 ppm level is shown in Figure 1, both SIM and scan traces. Each calibration level contained 16 PAHs, perylene-d12 (ISTD) and the three surrogate standards, 1,3-dimethyl-2-nitrobenzene, pyrene-d10, and triphenyl phosphate.

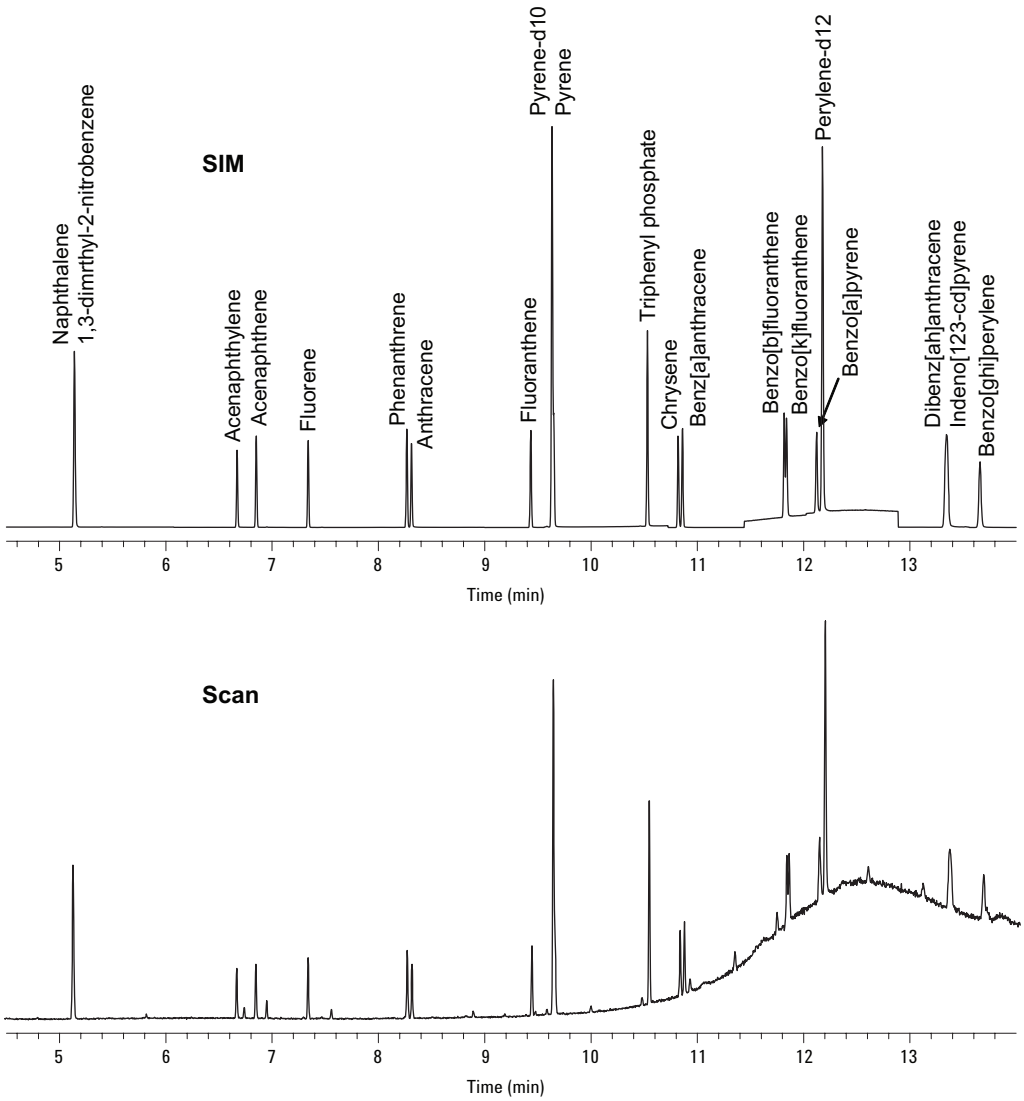

Figure 1. Sixteen PAHs at 0.2 ppm each with surrogates and ISTD at 1.0 ppm each, using synchronous SIM/scan mode.

The RRF (relative response factor) was calculated automatically for each compound at each level by the GC/MSD ChemStation software. Linearity was determined by calculating the %RSD (percent relative standard deviation) of the RRFs across the calibration range for each compound. This is also done automatically by the software in conjunction with Excel.

Linearity is excellent with the average of all %RSDs = 6 %. This compares favorably with other methods that are SIM only or those that only calibrate down to 0.1 ppm.

There were 5.55 SIM cycles/s and 5.55 scans/s acquired throughout the run. This yields 11 SIM data points and 11 scan data points across a typical peak.

Full scan data are also available for further PAH confirmation using library searching. Figure 2 shows a full scan spectrum from benzo[ghi]perylene, together with its library match. Unknown peaks for which SIM data were not acquired can also be library searched. A more reliable, faster method for identifying all the peaks is the use of Deconvolution Reporting Software [4].

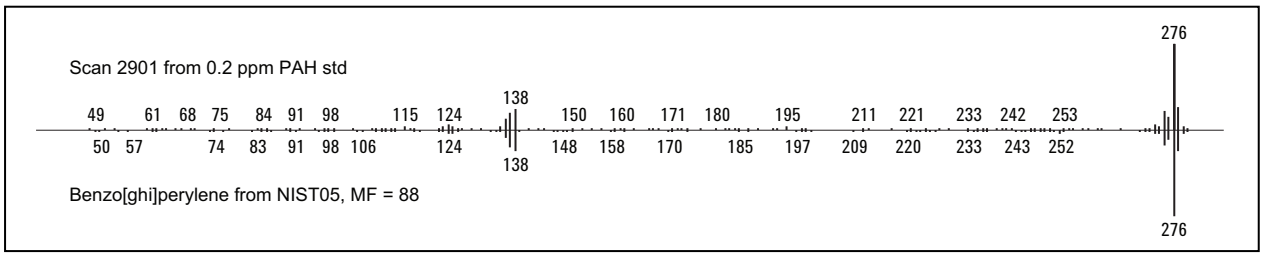

Figure 2. Spectrum from scan at 13.662 min with NIST05 Library match.

Conclusions

The 6890/5975 inert shows much improved response and peak shape for PAHs due to the inert source material and higher allowable source temperature. This improved response gives better linearity across the calibration range. Analysis of PAHs can be accomplished using synchronous SIM/scan data acquisition over a calibration range of 0.01 ppm to 10 ppm, while maintaining performance similar to SIM methods. Sensitivity of SIM is achieved while providing full scan data for confirmation of PAHs and identification of unknowns in a single run.

References

1. Mike Szelewski, “Full Scan Low Level Polynuclear Aromatic Hydrocarbon Analysis using the Agilent Technologies 6890/5973 inert Gas Chromatograph/Mass Selective Detector”, Agilent Technologies, publication 5989-0264EN, www.agilent.com/chem.
2. K. Weiner, N. Mata and P. Wylie, “Retention Time Locking with the G1701BA MSD Productivity ChemStation”, Agilent Technologies, publication 5968-3433E, www.agilent.com/chem.
3. Chin-Kai Meng, “Improving Productivity with Synchronous SIM/Scan”, Agilent Technologies, publication 5989-3108EN, www.agilent.com/chem.
4. Philip L. Wylie, Michael J. Szelewski, Chin-Kai Meng, and Christopher P. Sandy, “Comprehensive Pesticide Screening by GC/MSD using Deconvolution Reporting Software”, Agilent Technologies publication 5989-1157EN, www.agilent.com/chem.

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